



oby - Retraction between *dimethyl aniline*

THE REACTION BETWEEN DIMETHYL ANILINE
AND
BENZENE SULFONYL CHLORIDE

BY

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1918

1918
W.94

UNIVERSITY OF ILLINOIS

.....June 1.....1918..

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

.....Norman William Wroby.....

ENTITLED.....The Reaction between Dimethyl Aniline and Benzene.....

.....Sulphonyl Chloride.....

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF.....Bachelor of Science in Chemical Engineering.....

.....Oliver Kamm.....

Instructor in Charge

APPROVED:.....W. A. Noyes.....

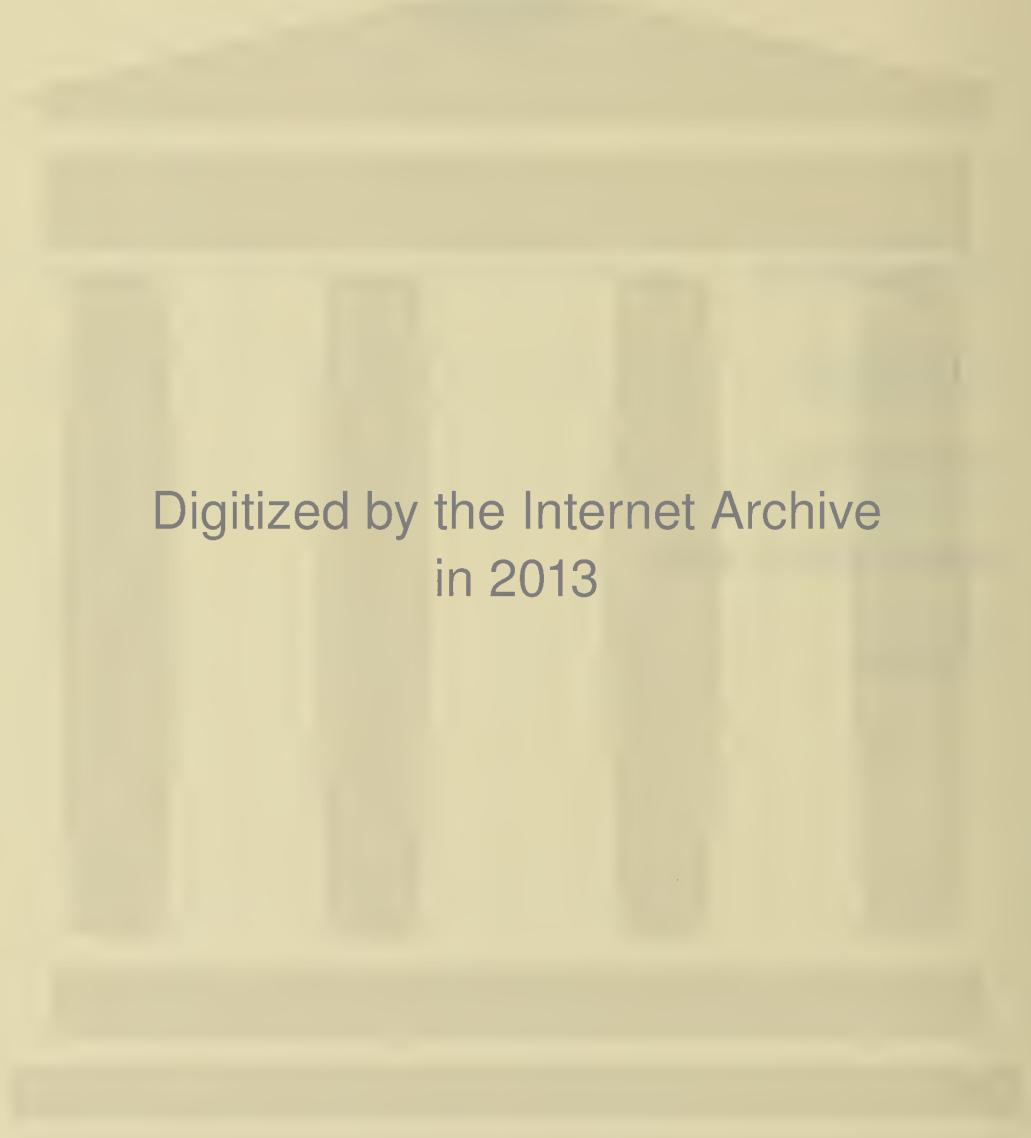
HEAD OF DEPARTMENT OF.....Chemistry.....

This problem was undertaken at the suggestion of Dr. Oliver Kamm. The author wishes to express his appreciation for the courtesies extended and the valuable assistance he has given.



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THE REACTION BETWEEN DIMETHYL ANILINE AND
BENZENE SULFONYL CHLORIDE

INTRODUCTION.

Benzene sulfonyl chloride has considerable application in chemistry, one important use being to distinguish between the three classes of amines, primary, secondary and tertiary. This application is generally known as the Hindberg test for amines (Ber. 23 2962). With primary amines, benzene sulfonyl chloride gives benzene sulfamides ($C_6H_5SO_2HN R$) which are soluble in alkali and precipitated with acid. Secondary amines react to give benzene sulfamides, mostly solid, crystalline precipitates which are insoluble in alkali or acid. Tertiary amines remain unaffected. The reactions between amines and benzene sulfonyl chloride are carried out in alkaline solution so that the alkyl sulfamides produced by primary amines remain in solution while the alkyl sulfamides resulting from secondary amines separate out. Tertiary amines do not react and remain with the alkyl sulfamides from secondary amines.

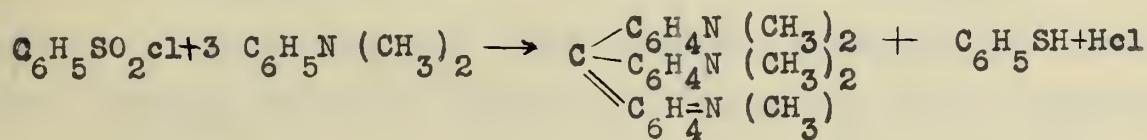
In the reaction between benzene sulfonyl chloride and dimethyl aniline, a blue dye-stuff is produced along with a basic compound and a sulfamide. Aromatic sulfonyl chlorides with dimethyl aniline give this blue product with the formation of a basic compound and a compound reported to be a sulfone.

Dimethyl aniline, therefore, is an exception to the general reactions of tertiary amines with benzene sulfonyl chloride and interferes with the Hindberg test for amines. It also causes con-

siderable trouble in the quantitative determination of amines as is shown in the Ph. D. theses of J. W. Howard, University of Illinois 1915, E. M. A. Chandler, University of Illinois 1917.

HISTORICAL

Several investigators have worked with dimethyl aniline, some studying the general reactions between dimethyl aniline and sulfonyl chlorides while others studied the oxidation of dimethyl aniline. The earliest workers had in view the production of the blue dye-stuff or methyl violet from dimethyl aniline in order to replace the use of the expensive iodine in the preparation of rosaniline. All of this work was done before Hindberg's test for amines was worked out. The first investigator to work on the reaction of dimethyl aniline and benzene sulfonyl chloride was W. Michler (Ber. X 1742) who explains that the blue dye-stuff is basic and is decolorized or bleached by mineral acids. He did not carry out any tests on the products formed. Two years latter H. Hassencamp published a paper (Ber. 12: 1275) entitled, "A New Method of Preparing Methyl violet". He treated one part of benzene sulfonyl chloride with three parts of dimethyl aniline and heated the solution on a water bath. The blue-violet dye-stuff was produced immediately. Upon treating the blue mass with water, thiophenol separated out. Hassencamp states that there is little doubt but that the reaction proceeds as follows:



No chemical tests were made for thiophenol or for methyl violet. He concludes that possibly a methyl group is oxidized from dimethyl aniline and this has a reducing effect on the sulfonyl chloride.

This same year another paper by W. Michler was published which was on the general subject of the behavior of sulfonyl chlorides toward amines. (Ber. XII 1791). He carries out the reaction by warming two molecules of dimethyl aniline on a water bath and slowly adding a molecule of benzene sulfonyl chloride. The reaction took place immediately. The products formed were tetramethyldiaminodiphenyl methane, dimethyldiaminodiphenylsulfone and a small quantity of blue dye-stuff. He obtained similar results by treating α -or β -naphthalenesulfonyl chloride or p-toluenesulfonyl chloride with dimethyl aniline. In each case tetramethyldiaminodiphenyl methane and the corresponding naphthalene or toluenedimethyldiaminodiphenylsulfones were formed. The reactions between sulfonyl chlorides and dimethyl aniline are not the only reactions which give this blue product. A number of workers have treated dimethyl aniline with inorganic reagents and have produced the blue dye-stuff. Louth was the first investigator to discover a process for producing methyl violet from dimethyl aniline, which heretofore had been made from rosaniline. A mixture of a copper salt (nitrate, sulphate, chloride) sodium chloride, sand, dimethyl aniline and an acid, is heated to 40° - 60° when the blue product immediately forms. The mass is extracted with water and the dye-stuff precipitated with sodium chloride.

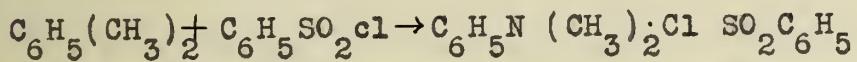
Fisher has shown that during the oxidation of dimethyl aniline, formaldehyde and formic acid are produced (Ber. 1878 11, 2098, 1883 16 2909) and explains the formation of the dye-stuff by suggesting that one of the methyl groups of dimethyl aniline is

eliminated, yielding formaldehyde, while mono-methyl aniline remains. The formaldehyde then condenses with di- and mono-methyl aniline giving derivatives of diphenyl methane and these oxidized in the presence of excess of bases, form~~s~~ di-tetra, and penta methyl para-rosanilines.

W. Michler (Ber. 1876 IX 400, 716) finds that by treating dimethyl aniline with carbonyl chloride, the blue dye-stuff is formed and on analysis of this blue mass, found diaminobenzophenone or Michler's ketone as one of the constituents. H. A. Brunner and Brandenberg (Ber. 1878 XI 697) have produced the dye-stuff by oxidizing dimethyl aniline with bromine water. The theory of the production of blue dye-stuff from dimethyl aniline seems to be the same in all the papers, that is, that dimethyl aniline is oxidized and a methyl group is freed which is oxidized and through condensation with mono- and di-methyl aniline, produces methyl violet.

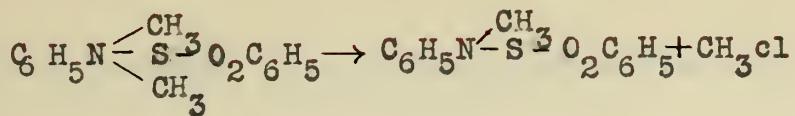
THEORETICAL

In the reactions between dimethyl aniline and benzene sulfonyl chloride, the first step is possibly the formation of an addition product.

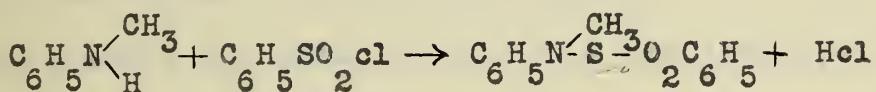
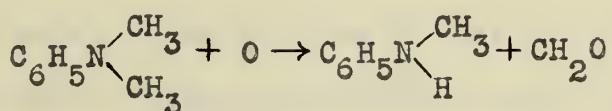


It has been found by Dehn (J. Am. Chem. Soc. 39, 2444) that in the reaction of tertiary amines with benzene sulfonyl chloride, addition products are formed.

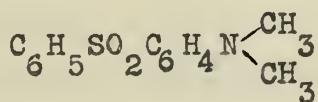
The next step in the reaction is the splitting off of methyl chloride from the addition product leaving methylphenyl sulfamides.



This compound has been isolated and identified in the present work. Methylphenylsulfamide is also formed by the reaction of mono-methyl aniline and benzene sulfonyl chloride. The mono-methyl aniline being produced by the oxidation of a methyl group from dimethyl aniline.



The melting point of this compound obtained from pure dimethyl aniline has been found to be 78°C . Pure methylphenyl sulfamide was made from mono-methyl aniline and benzene sulfonyl chloride and the melting point of the mixture of pure compound and that isolated from the reaction, remained at 78°C . W.Michler (Ber. XII 1791) claims to have obtained dimethylaminodiphenyl sulfone,



melting at 82°C . Carbon and hydrogen determinations were made on this compound by Michler, and the results obtained checked rather closely with the calculated percentage of carbon and hydrogen. But the percentage of carbon and hydrogen in methylphenyl sulfamide is practically the same as that in dimethylaminodiphenyl sulfone, so that Michler's results are not very different from those given by

methylphenyl sulfamide. The percentage of carbon and hydrogen is as follows:

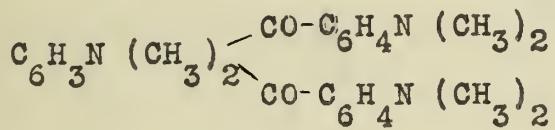
dimethylaminodiphenyl sulfone		methylphenyl sulfamide
calculated	Michler	calculated
C 64.36	64.23	63.16
H 5.74	5.78	5.26

The difference in the melting points of methylphenyl sulfamide and the melting point obtained by Michler can be accounted for in that his compound may not have been pure.

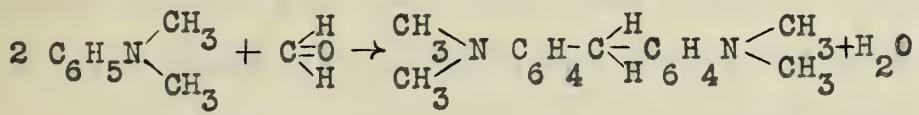
As regards the solubility of the two compounds in acid, dimethylaminodiphenyl sulfone should be soluble, being a basic compound while methylphenyl sulfamide is not. Michler's method of obtaining dimethylaminodiphenyl sulfone was by dissolving the basic compounds with acid and his sulfone remained as a residue. Since it is known that dimethylaminodiphenyl sulfone should be soluble in acid, Michler could not have had that compound but must have had methyl phenyl sulfamide which is insoluble in acids.

It is very probable that in the reaction between dimethyl aniline and toluene sulfonyl chloride, Michler did not obtain toluene dimethylaminophenyl sulfone melting at 95° C but methyl toluene sulfamide melting at 94°-95° C. Toluene di-methylaminophenyl sulfone should have basic properties and be soluble in acid while methyl toluene sulfamide is not soluble in acids. Michler claims to have obtained his compound as a residue from acid solution showing it to be non-basic. The percentage of carbon and hydrogen in toluene dimethylaminophenyl sulfone and methyl toluene sulfamide is practically the same. Since the melting points of the two compounds are the same

and methyl toluene sulfamide is not soluble in acid while toluene dimethylaminophenyl sulfone should be soluble, all indications are that Michler had the sulfamide instead of the sulfone. In the literature, the only reference made to dimethylaminodiphenyl sulfone is to the work of Michler and the results of the present work show that it is not the sulfone but methylphenyl sulfamide and since similar contradictions appear in reference to toluene dimethylaminophenyl sulfone, it seems that in the general reaction between dimethyl aniline and aromatic sulfonyl chlorides, sulfamides and not sulfones are produced. It can be shown that in Michler's work (Ber. 9 716) with dimethyl aniline and carbonyl chloride, the compound obtained



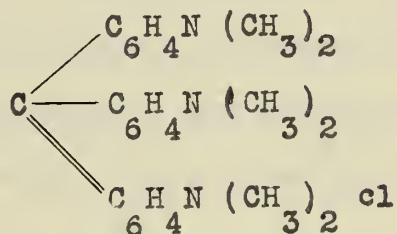
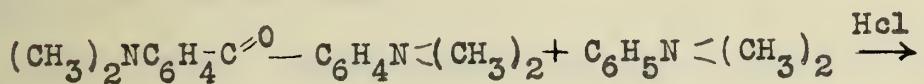
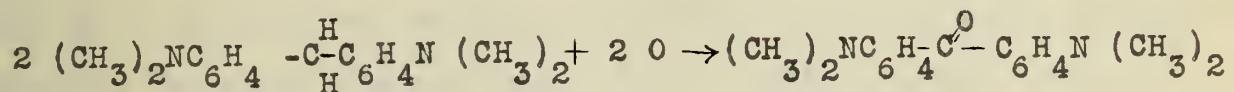
melting at 122°C might also be symmetrical di-methyl-diphenyl urea which also melts at 122°C. The latter substance is non-basic and Michler reports his tri-amino compound to be non-basic. The formaldehyde and formic acid resulting from the oxidation of di-methyl aniline with that produced by the oxidation of methyl chloride, reacting with dimethyl aniline, gives tetramethyldiaminodiphenyl methane.



This compound has been isolated in the present work, and identified by its melting point. (91°c.) Michler also found this compound and identified it.

The formaldehyde present condenses with dimethyl aniline

to give derivatives of diphenyl methane, which in the presence of an excess of bases and an oxidizing agent will give methyl derivatives of para-rosaniline. These compounds are blue dye-stuffs.



EXPERIMENTAL WORK

The first work on the reaction between dimethyl aniline and benzene sulfonyl chloride was not so much on the separation of the products formed but rather on the method of carrying out the reaction. When one part of benzene sulfonyl chloride was added to two parts of dimethyl aniline and the mixture was slightly heated, a violent reaction took place, resulting in the production of a blue oily mass. When the reaction was once started enough heat was generated to continue the reaction. The blue mass was treated with a dilute solution of sodium hydroxide to decompose the excess benzene sulfonyl chloride and the excess dimethyl aniline was removed by steam distillation. The reddish-brown oily mass remaining after steam dis-

tillation turned to a blue color on the addition of hydrochloric acid. The oily mass was separated from the solution and washed with water. Several qualitative tests were carried out. Sodium decomposition test showed the presence of sulphur. Taking the oily mass up in alcohol and bubbling dry hydrochloric acid gas through the solution the color changed from blue to reddish-brown. No precipitation takes place.

Several quantitative tests were made in order to determine the ratio of nitrogen to sulphur in the blue mass. The blue mass was taken up in alcohol and again removed by evaporation in order to have a homogeneous mass for analysis. The nitrogen was determined by the Kjeldahl method and the sulphur by the method of Carius. The results were as follows:

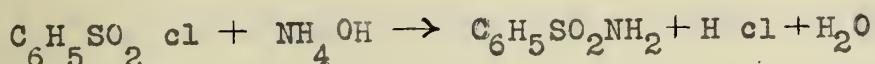
per cent nitrogen	per cent sulphur
6.71 6.73	6.57 7.28

A fresh sample of the blue dye-stuff was prepared as explained above and nitrogen analysis were carried out. The results were 6.29 and 6.36 per cent nitrogen showing that the nitrogen content was quite constant. The above results also show that the percentage of sulphur and nitrogen was practically the same and that there were two atoms of nitrogen to one of sulphur. The method of attack for the separation of the constituents of the blue mass or rather the identification of the products of the reaction of dimethyl aniline and benzene sulfonyl chloride was similar to that of Michler. Dimethyl aniline was heated on a water bath and benzene sulfonyl chloride slowly added. A blue oily mass was obtained. Heating this blue mass on a water bath for a few minutes and then adding an excess of ammonium hydroxide, a deep pink solution appeared over the

blue mass. The ammonium hydroxide decomposed the excess benzene sulfonyl chloride and by steam distillation the excess di-methyl aniline was removed. Separating the oily residue from the alkaline solution and treating it with a dilute solution of hydrochloric acid, a residue remained. The acid dissolved all the basic compounds and left a crystalline residue contaminated with the blue dye stuff. This was recrystallized from alcohol several times in order to remove the dye. The compound was white when pure and melted at 78°c . It was considered at the time that the compound contained impurities because Michler isolated a compound this same way and it melted at 82°c . The hydrochloric acid filtrate from above was made alkaline with ammonium hydroxide in order to precipitate the basic compounds. A very small precipitate formed but it was not large enough to work with.

More blue dye-stuff was produced as explained above except that two parts of dimethyl aniline and one part of benzene sulfonyl chloride was used. The object of varying the ratio of dimethyl aniline to benzene sulfonyl chloride was to produce if possible less dye-stuff and more of the other products of the reaction. The blue dye-stuff contaminated the products and increased greatly the difficulty of separation. The blue mass was treated with hydrochloric acid and a residue remained which on purification melted at 78°c . Making the acid filtrate alkaline with ammonium hydroxide and steam distilling to drive off the excess dimethyl aniline an oily mass remained which crystallized on cooling. This was contaminated with dye-stuff but melted at 86°c . This was undoubtedly tetramethyl-diaminodiphenyl methane but as the precipitate was small not enough remained to continue the purification and identification.

Equal parts of dimethyl aniline and benzene sulfonyl chloride were brought into reaction. On treating the bluemass with ammonium hydroxide, a precipitate formed. This was separated from the solution and on purification, it melted at 152°c. This was possibly benzene sulfone amide resulting from the reaction of ammonium hydroxide and benzene sulfonyl chloride.



Nitrogen analysis were made on this compound in order to identify it. The results averaged 10.24 per cent nitrogen. The percentage of nitrogen in benzene sulfone amide is 8.9 and its melting point is 150°c. There is a possibility that the compound may have been isotetramethyldiaminobenzophenone which melts at 152°c and has 10.44 per cent nitrogen. From the results of the nitrogen analysis it seems that the compound was isotetramethyldiaminobenzophenone.

The reaction was then carried out in a solution of benzene to see whether a solvent would decrease the amount of dye-stuff. Sodium hydroxide was used instead of ammonium hydroxide to see if the compound melting at 152°c would again precipitate.

Dimethyl aniline was added to thirty cubic centimeters of benzene and the solution was refluxed with benzene sulfonyl chloride for two hours. The blue dye-stuff was produced. Sodium hydroxide was added to decompose the excess benzene sulfonyl chloride and the mixture was steam distilled to remove the benzene and excess dimethyl aniline. Treating the blue oily mass with hydrochloric acid, a residue remains, melting at 78°c. The hydrochloric acid filtrate was then made alkaline with sodium hydroxide. A precipitate formed which melted at 152-154°c. This made it seem as

if the compound was isotetramethyldiaminobenzophenone because no ammonium hydroxide was used to form benzenesulfone amide.

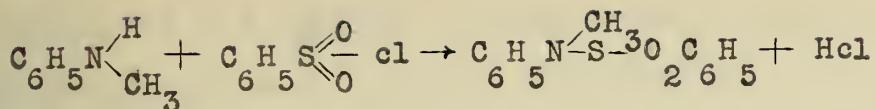
Tetramethyldiaminodiphenyl methane was then prepared to take the mixed melting points with the compound isolated that melted at 90°c and also to determine whether it was possible to obtain isotetramethyldiaminobenzophenone from the oxidation of tetramethyldiaminodiphenyl methane or from its reaction with benzene sulfonyl chloride since both are present in the mixture resulting from the reaction of benzene sulfonyl chloride and dimethyl aniline.

The diphenyl methane derivative was produced by adding 26 grams of dimethyl aniline to 30 grams of concentrated hydrochloric acid, the flask being kept cool all the time. 9 grams of formaldehyde (40% Soln.) were added and the mixture was refluxed for five hours at the boiling point. The slightly colored solution was diluted with water and made alkaline with sodium hydroxide. The excess dimethyl aniline was removed by steam distillation. The oily mass remaining crystallized on cooling. It was recrystallized from alcohol and melted at 90-91°c. Yield was 20 grams.

Reaction between the diphenyl methane derivative and benzene sulfonyl chloride was carried out to see whether the iso derivative of Michler's ketone or Michler's ketone itself could be produced. Adding benzene sulfonyl chloride to tetramethyldiamino-diphenyl methane and warming gently the blue dye was obtained. Sodium hydroxide was added and the mixture was steam distilled. The oily blue mass disappeared during steam distillation and the solution took on a green color. During steam distillation, the solution became acid and when sodium hydroxide was added, an oily mass separated and on cooling crystallized. It melted at 89°c and

appeared to be excess tetramethyldiaminodiphenyl methane. Taking a mixed melting point with the original diphenyl methane derivative, verified the result. Since it was a problem in itself to produce either the iso derivative or Michler's ketone, efforts were made to eliminate its appearance in the reaction between dimethyl aniline and benzene sulfonyl chloride.

Dimethyl aniline and benzene sulfonyl chloride were mixed in equal proportions and shaken with distilled water for twenty minutes. On standing over night the oily mass became green and a white pasty mass separated. The solution became green due to the acid, resulting from the reaction, adding on the blue dye formed. Cooling this white mass with ice it finally crystallized and on purification it melted at 78°c . Making the slightly acid filtrate alkaline with sodium hydroxide, a precipitate formed which melted at 89°c . Taking a mixed melting point with the pure tetramethyl-diaminodiphenyl methane prepared above, there was no variation in the melting point, so that the compound obtained was proven to be tetra-methyldiaminodiphenyl methane. In most all of the reactions between dimethyl aniline and benzene sulfonyl chloride, the compound melting at 78°c was isolated and it was impossible to change the melting point by further purification of the compound. Since methylphenyl sulfamide melts at 78°c and is not soluble in acid, it has properties similar to the compound from the reaction and it was prepared to use in identifying the unknown compound. Methylphenyl sulfamide was prepared by treating mono-methyl aniline with benzene sulfonyl chloride.



A small amount of dilute alkali was added to decompose the excess benzene sulfonyl chloride and the precipitate was filtered off and washed. After recrystallization with alcohol, it melted at 78°C . The unknown compound melting at 78°C was mixed with the pure methylphenyl sulfamide and there was no change in the melting point showing the two compounds to be identical.

To be sure there was no mono-methyl aniline in the dimethyl aniline, it was tested with acetic anhydride. Five cubic centimeters of dimethyl aniline were treated with acetic anhydride. There was no rise in temperature. Each 1° rise in temperature is an indication of the presence of $\frac{1}{2}$ per cent of mono-methyl aniline. The dimethyl aniline was also treated with methyl iodide so that any mono-methyl aniline present would be converted into dimethyl aniline. For each mole of dimethyl aniline, one-fourth mole of methyl iodide was added. The mixture was refluxed for four hours and then poured into water. The dimethyl aniline separated out. It was washed three times with ten per cent sodium hydroxide solution and dried over stick sodium hydroxide. It was then distilled.

Using this pure dimethyl aniline in the reaction with benzene sulfonyl chloride, methylphenyl sulfamide was again produced. The filtrate from the acid treatment was made alkaline with sodium hydroxide. A fine precipitate formed which on purification melted at $89-90^{\circ}\text{C}$. This was tetramethyldiaminodiphenyl methane.

Since it was found that in the reaction between dimethyl aniline and benzene sulfonyl chloride, methylphenyl sulfamide was produced and not dimethylaminodiphenyl sulfone, it was decided to

investigate the reaction between dimethyl aniline and α or β naphthalene sulfonyl chloride to see if the corresponding methyl naphthyl sulfamides could be obtained in place of the naphthalene-dimethylaminophenyl sulfones. Methyl α -naphthyl sulfamide had not been prepared before so it was prepared in this work by treating mono-methyl aniline with α -naphthalene sulfonyl chloride. A pasty mass resulted which crystallized on standing. It was purified and melted at 65° . It is possible that the compound was not pure but it was impossible to get it to melt at a higher point after many recrystallizations. Treating β -naphthalene sulfonyl chloride with mono-methyl aniline, a compound is obtained melting at 102° c. It is possible that Michler had a mixture of methyl α -naphthyl sulfamide melting at 65° c and methyl β -naphthyl sulfamide melting at 102° c, because the compound he isolated melted at 91° c.

SUMMARY

The results of the present work show that in the reaction between dimethyl aniline and benzene sulfonyl chloride, addition and oxidation products are obtained which result in the formation of methylphenyl sulfamide, tetramethyldiaminodiphenyl methane, iso-tetramethyldiaminobenzophenone and a blue dye-stuff, methyl violet.

The methylphenyl sulfamide is produced by the formation of a direct addition product between dimethyl aniline and benzene sulfonyl chloride, followed by the splitting off of methyl chloride. Tetramethyldiaminodiphenyl methane is produced by the formaldehyde resulting from the oxidation of either dimethyl aniline or methyl

chloride, reacting with dimethyl aniline. The blue dye is produced by the condensation of formaldehyde with dimethyl aniline to give tetramethyldiaminodiphenyl methane which in the presence of bases and an oxidizing agent gives methyl derivatives of para-rosaniline.

The formation of methylphenyl sulfamide in the present work contradicts the work of Michler, who claims to have obtained dimethyl aminodiphenyl sulfone. The only reference in the literature to the above sulfone is to the sulfone obtained by Michler and this has been shown to be methylphenyl sulfamide. The same is true of toluene dimethylaminophenyl sulfone obtained by Michler in the reaction between dimethyl aniline and toluene sulfonyl chloride. From the knowledge obtained in the literature, there are strong indication that Michler obtained methyl toluene sulfamide and not toluene dimethylaminophenyl sulfone. These results indicate that in the general reaction between dimethyl aniline and aromatic sulfonyl chlorides, sulfamides and not sulfones are produced.

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